

# SPECTROSCOPIC CONSTANTS OF MOLECULES

## III. REGULARITIES IN VIBRATION FREQUENCIES IN A MOLECULAR GROUP

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**ABSTRACT.** Regular variation of vibration frequency  $\omega_e$  and force constants  $k_e$  in a molecular group has been studied. It is shown that, in a molecular group, if the  $\omega_e$  of the series of molecules of a metallic element are plotted against the  $\omega_e$  of the corresponding molecules of another metallic element, straight lines are obtained. Unknown  $\omega_e$  have been predicted.

### INTRODUCTION

With the gradual development of molecular spectrum studies, it became evident that some sort of classification was necessary.

Clark (1934 *a,b*; 1935*a*) divided the diatoms into periods which were designated as KK, KL, KM etc., the letters indicating the closed electronic shells of the component atoms. Several workers have investigated diatoms on this basis and found fruitful regularities in diatoms belonging to the same period (Clark, 1934*a*, 1935*b*, 1936, 1938, 1941; Huggins, 1935, 1936; Wu and Chao, 1947; Allen and Longair, 1935 and others).

On the other hand regularities have also been traced in diatoms on basis of the Periodic Table. The diatoms can be classified depending on the type of linkage. Suppose a diatom consists of two atoms, one belonging to, say IV*b* group (C, Si, Ge, Sn, Pb) and the other to VII *b* group (F, Cl, Br, I, At) of the Periodic table. Examples of such diatoms will be CF, Si Cl, CCl, etc. Such diatoms have similar linkage. In the case cited they all have  $^2\Pi$  ground state. Investigations on these lines have been made by Mecke (1927), Carrelli and Trautteur (1937), Lovera (1951) and others. Recent work of Pritchard and Skinner (1951) shows that excellent results are obtained for Badger's rule on group classification.

Sutherland (1940) found regularities on both classification, period as well as group.

In view of the fact that in Periodic Table regular variations of properties are found in groups as well as in periods, it is easy to see that regularities should exist in molecular 'periods' as well as in 'groups'. It would be appropriate to say that the properties of a diatom are determined both by the considerations of the 'period' and the 'group' to which it belongs.

In the present paper regularities in the ground state vibration frequencies of diatoms belonging to the same group have been studied. The groups will be denoted by the two subgroups of the Periodic Table to which the constituent atoms belong. Thus  $4b-6b$  group denotes CO, CS, .....type of molecules. It is possible by these investigations to estimate unknown  $\omega_e$  values ; they also point out anomalous values which may give a clue to the abnormalities existing in the electronic states.

If we arrange the vibration frequencies of molecules as shown in Table I, which shows  $4b-6b$  group of molecules, certain regularities become apparent.

TABLE I

Vibration frequency (in  $\text{cm}^{-1}$ )

	O	S	Se	Te
C	2170.2	1285.1	1036	$\sim 875$
Si	1242	749.5	580	481.2
Ge	985.7	575.8	406.8	323.4
Sn	822.4	487.68	331.2	259.5
Pb	721.8	428.14	277.6	211.8

The vibration frequency is seen to decrease horizontally towards right hand side and vertically downwards. Very similar behaviour is found for the force constants as Table II shows.

TABLE II

Force constant  $k_e$  (in Des. =  $10^5$  dynes/cm)

	O	S	Se	Te
C	19.02	8.488	6.586	4.945
Si	9.246	4.938	4.094	3.130
Ge	7.526	4.358	3.743	2.776
Sn	5.615	5.536	3.566	2.439
Pb	4.556	2.992	2.595	2.086

An examination of the  $\omega_e$  and  $k_e$  values of molecules of various groups showed that such regularities exist in all group for which data are available, except  $1a-7b$  group. This group will be discussed later on.

If the vibration frequencies of the diatoms of a group having the same metallic atom are taken on abscissa and the vibration frequencies of other

diatoms of the same group having some other metallic atom are plotted against corresponding non-metallic elements, a straight line is obtained. For example, the vibration frequencies of SrF, SrCl, SrBr, SrI are linear with the vibration frequencies of CaF, CaCl, CaBr, CaI. This relationship has been examined for various groups for which data are available in figures 1-9. Deviations from a strictly linear relationship are without doubt real, however the discrepancies are of a minor nature. As the deviations seem to vary systematically in going down a group it is convenient to take the middle element in a group on the abscissa (thus Ga in IIIb group), but this is not very essential. It is best to choose that series as abscissa for which well established  $\omega_e$  values are available. When only two points are available, the straight line has been drawn taking into consideration how the points on other lines are distributed. Thus the carbon line (figure 7) has been drawn, in analogy with other lines, such that the fluoride point is a little above and the chloride point a little below.

#### DATA

Excepting for the following molecules, for which more accurate values have been reported, the data have been taken from Herzberg (1950) and Rosen (1951).

TABLE III

Group	Molecules	Reference
1a-7b	KF, KCl, KBr, KI, RbF, RbCl, RbBr, RbI, CsF, CsCl, CsBr, CsI	Barrow and Caunt (1953)
1b-6b	AgO	Uhler (1953)
3b-7b	GaF, InF	Welti and Barrow (1952), Barrow, Jacquest and Thompson (1954)
5b-6b	AsS, SbS, BiS, SbSe, SbTe, BiSe, BiTe	Sur (1952) Sharma (1950, 1954)

#### DISCUSSION

It will be noticed that in general the linear relationship is well obeyed. As mentioned earlier, there are small and somewhat regular variations from the straight line. Usually the slope decreases as we go down a group.

Table IV lists the predicted values from the graphs for such molecules which have not been investigated or whose reported values of  $\omega_e$  seem to be doubtful. The actual values can be expected to be within 5% of these estimated values. Individual groups are discussed below.

TABLE IV

Group	Abcissa	Molecule	Estimated $\omega_e$	Remarks
1a-7b	K	NaI <sup>2</sup>	465	Discrepancy
		CsI <sup>2</sup>	350	
1b-7b	Cu	AgI <sup>2</sup>	525	
2a-7b	Ca	RaI	160	
		BeBr	670	
		BeI	580	
2b-7b	Hg	ZnBr	280	Discrepancy
3b-7b	Ga	BI	570	
4b-7b	Pb	CBr	670	
		CI	570	
		SiI	340	
		GeI	230	
		SnI	190	
5b-6b	Bi	NSe	1000	
		NTe	880	
		AsSe	~700	
		AsTe	~660	
5b-7b	Bi	SbBr	225	
		SbI	175	

#### 1a-7b Group.

CsI<sup>2</sup> does not fall on the straight line. However, there is considerable difference between the values reported by different workers for this molecule—385 (spectroscopic, Barrow and Caunt—1953),  $270 \pm 30$  (radio frequency electric resonance spectrum—Trischka, 1948, 1949), 345 (theoretical value on a classical model—Rittner 1951). The graphical value 350 is very close to the value of Rittner. Barrow and Caunt also think that the spectroscopic value may be a little too high.

It is significant to note that the slope of sodium (Na) line is less than that of Rb, contrary to the behaviour of other molecules (only one more such example has been encountered - As).

A study of the  $\omega_e$  and  $k_e$  values of this group reveals interesting irregularities.

TABLE V

Vibration frequency

	F	Cl	Br	I
Li				450
Na		380	315	286
K	400	305	230	200
Rb	390	270	180	145
Cs	385	240	168	120

TABLE VI

Force constant  $k_e$  (in Des. =  $10^5$  dynes/cm)

	F	Cl	Br	I
Li				.7845
Na		1.186	1.041	.9378
K	1.205	1.019	.818	.704
Rb	1.361	1.076	.788	.633
Cs	1.151	.95	.83	.551

While the  $\omega_e$  values seem to be regular, such is not the case with the force constants. The  $k_e$  value for LiI is lower than that of NaI contrary to the expectation. It is interesting to note that the  $\omega_e$  (LiI) = 616 or  $k_e$  (LiI) = 1.57 calculated by Rittner on a classical model of alkali-halides would give the correct trend to the force constants. On the other hand, considerations based on similarities in iso-electronic molecules do not support a value greater than 500 (to be discussed in Part IV). The trend of  $k_e$  values for bromides suggests that for CsBr a lower value near .76 is to be preferred to the reported value .83. Figure 1 also supports a lower value. The force constants of fluorides increase as we pass from K to Cs, instead of decreasing. As all the three values have been reported by the same workers (Barrow and Caunt) using the same methods, it cannot be said

which value is more reliable. The theoretical values of Rittner,  $\text{KF} = 1.266$ ,  $\text{RbF} = 1.166$ ,  $\text{CsF} = 1.113$ , have the correct trend. The anomaly of  $\text{CsF}$  has been discussed above also.

It would be obvious from these considerations that the situation of  $\omega_e$  values of these diatoms is not very satisfactory. It should be remembered that the experimental investigation of these molecules is rather involved. The band systems arise from transitions from the stable ionic ground states to weakly bound upper states which dissociate into neutral atoms. These upper states are either purely repulsive, or have such shallow minima that their rotational and vibrational levels lie too close to be resolved. The bands are narrow and diffuse and it is very difficult to derive correct  $\omega_e$  values (Barrow and Caunt, 1953).

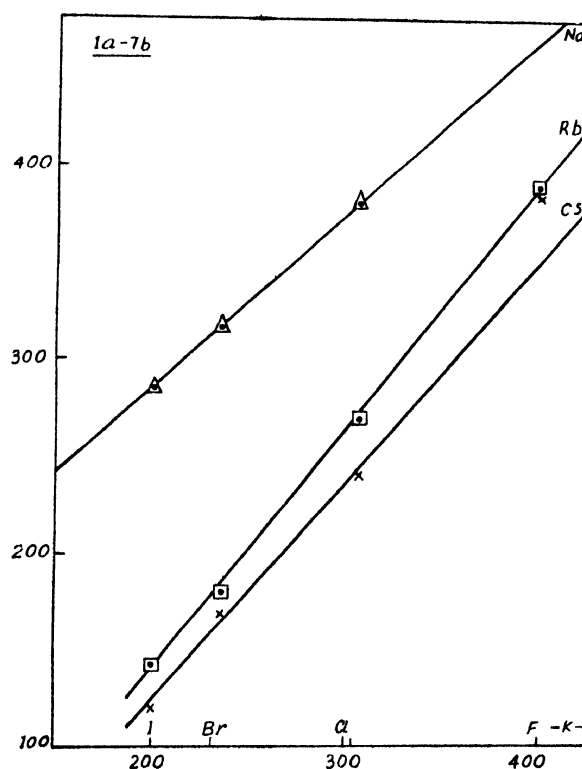


FIG. 1. 1a-7b Group

1b-7b Group (figure 2). Sufficient data for Au are not available. The straight line for Ag is satisfactory.

2a-7b Group (figure 3). The linearity is well obeyed.

2b-7b Group (figure 4). There is one discrepancy— $\text{ZnBr}$ .

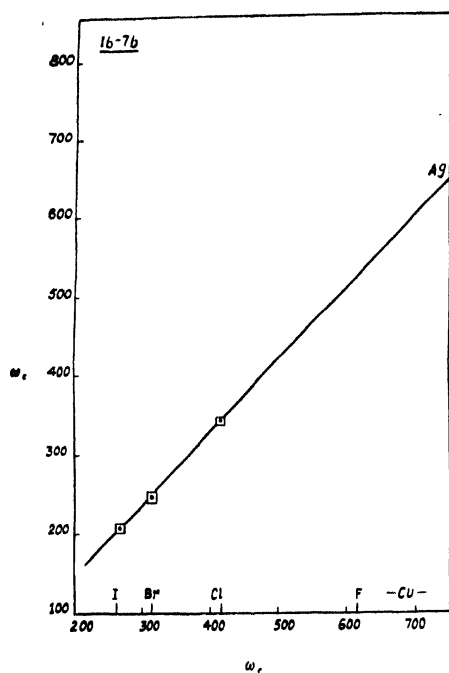


FIG. 2. 1b-7b Group

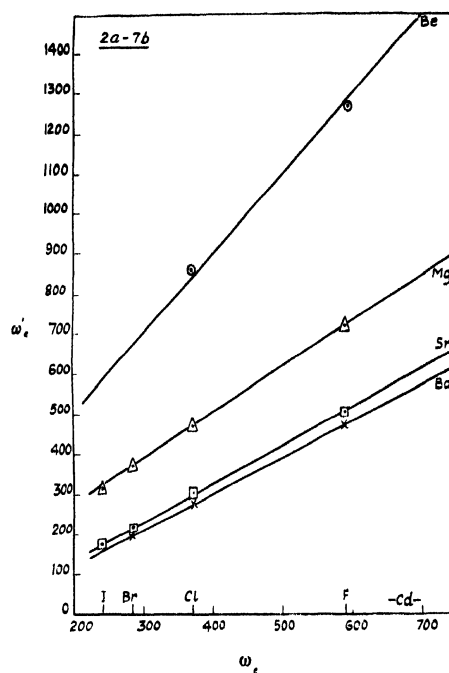


FIG. 3. 2a-7b Group

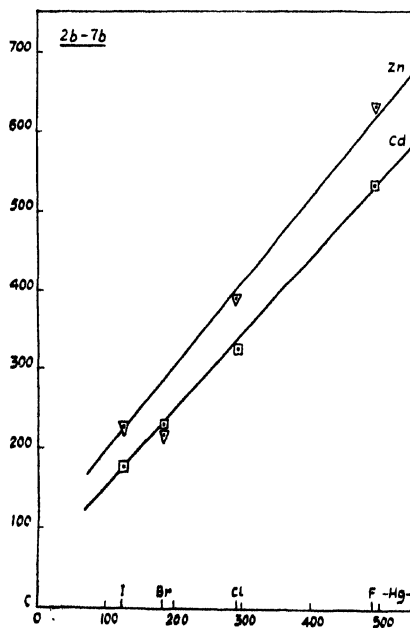


FIG. 4. 2b-7b Group

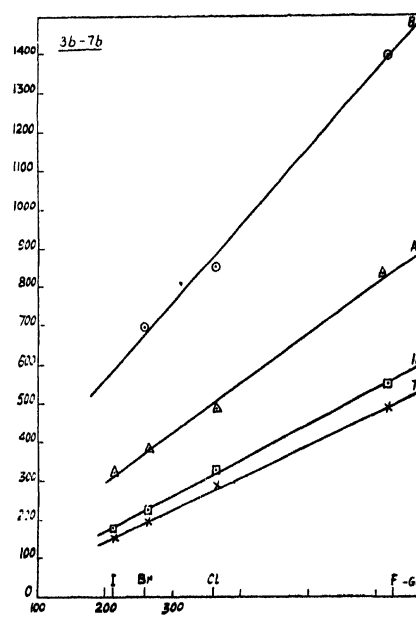


FIG. 5. 3b-7b Group

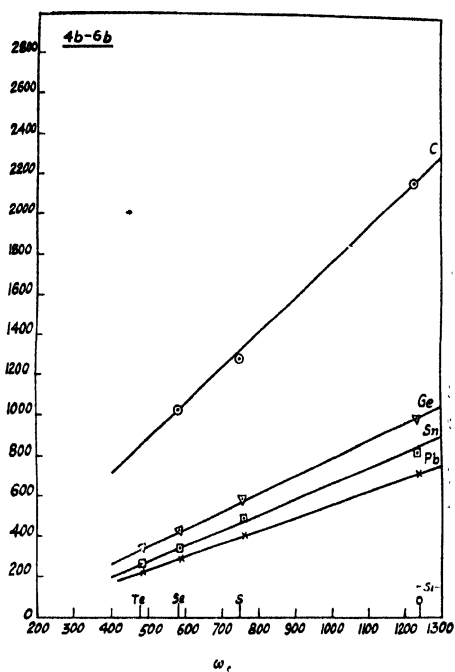


FIG. 6. 4b-6b Group

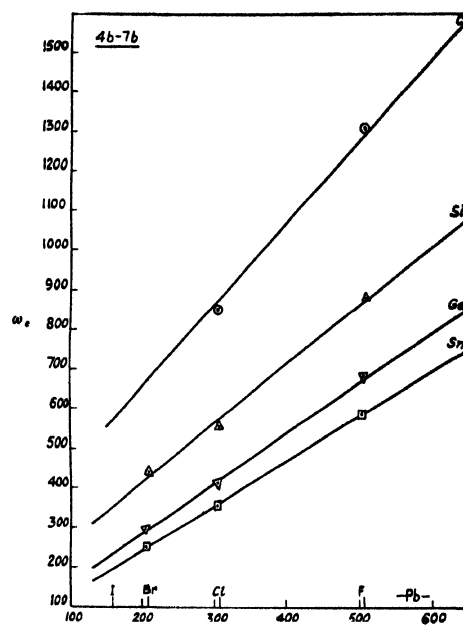


FIG. 7. 4b-7b Group

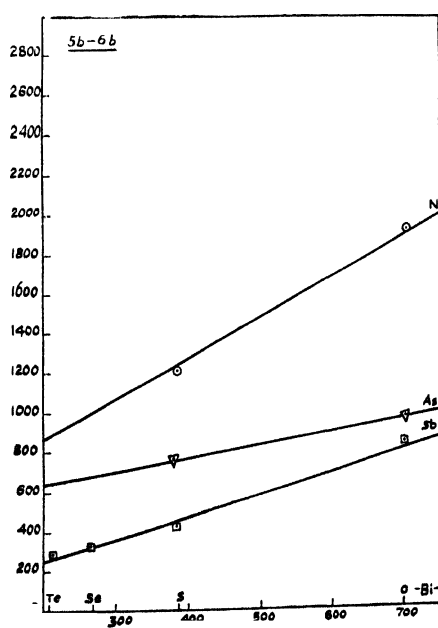


FIG. 8. 5b-6b Group

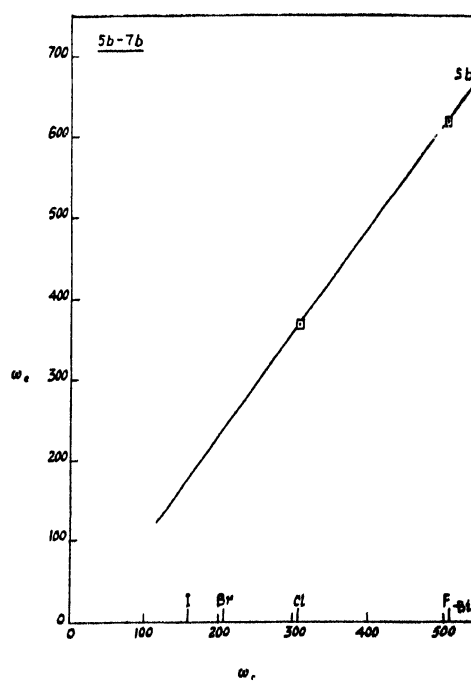


FIG. 9. 5b-7b Group



However, the experimental value of  $\omega_e$  of this diatom is not known correctly, even this is not certain whether the observed bands are due to ZnBr. An examination of the series ZnF-(630), ZnCl-(390.5), ZnBr-(220), ZnI-(223.4) shows that the experimental value is definitely in error.

*3b-7b, 4b-6b, and 4b-7b Groups* (figures 5, 6, 7). The straight lines are satisfactory.

*5b-6b Group* (figure 8). The slope of As line is lower than that of Sb line. As only two points are available for As, error in any of these is possible. If it is so, values for AsSe and AsTe will have to be modified accordingly. Further,  $k_r(\text{AsS})=7.78$ , comes out to be greater than  $k_r(\text{AsO})=7.266$  which is again anomalous. We will return to this point in part IV.

*5b-7b Group* (figure 9). Only two points for Sb are available. The predicted values for SbBr and SbI are given in Table IV.

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